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Syntheses of new rare-earth rhodium borocarbides

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Abstract

Single crystals of a new quaternary compound, $ErRh_2B_2C$, were obtained by the flux growth method using molten copper as a flux. The extracted crystals show golden-coloured luster and a maximum size of approximately $1 \times 1 \times 0.02$ mm^3. This compound has tetragonal symmetry and appeared to be a derivative of the $ThCr_2Si_2$-type; the lattice parameters are $a = 0.36848(2)$ nm and $c = 1.05520(3)$ nm. The electrical resistivity parallel to the a-b plane of the crystal decreases with decreasing temperature. The residual resistance ratio ρ (273 K)/ρ (1.5 K) is 1.38. No superconductivity was observed down to 1.5 K. The search for similar types of new compounds was performed using the arc-melting synthetic method. The new quaternary RRh_2B_2C compounds are obtained for R = La − Er (except Eu) and Y. The phase stability of RRh_2B_2C was discussed.

Keywords: $ErRh_2B_2C$; $ThCr_2Si_2$-type compound; Single crystal; Flux growth; Electric properties

Introduction

Studies have accelerated on R-M-B-C (R = rare earth element, M = transition element), encouraged by reports on borocarbides composed of four elements such as Y–Ni–B–C and Y–Pd–B–C; these compounds show high superconducting transition temperatures [1,2]. Although it is recognised that there are many interesting compounds among such quaternary systems in terms of the coexistence of magnetism and superconductivity, etc., efforts to systematically search for such compounds still seem to be insufficient.

This study is an attempt to synthesise new borocarbides in the system of Er–Rh–B–C using a molten metal flux growth method and aims to synthesise compounds directly as single crystals. As a result, the new compound $ErRh_2B_2C$ is obtained. The crystal

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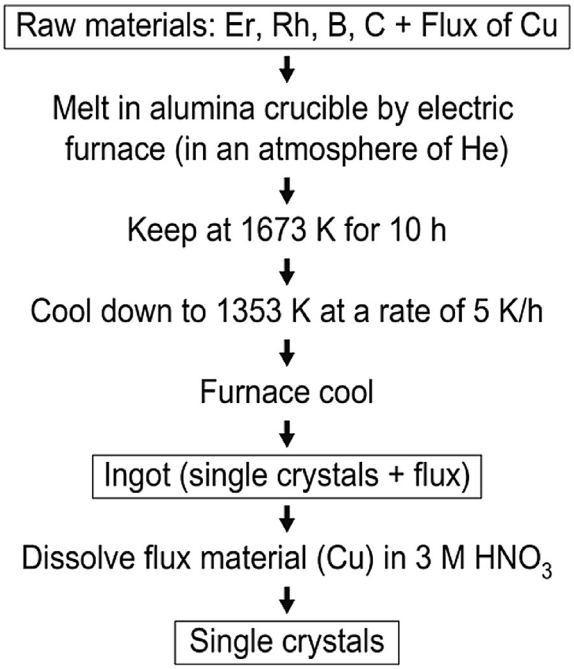

Fig. 1. The growth procedure of the single crystals of quaternary borocarbide in the Er–Rh–B–C system by the flux method using molten Cu as a flux.

structure and electronic properties of the new compound are analysed extensively using the arc-melting synthetic method. The phase stability of the new borocarbides is determined.

Experimental details

The materials used in the flux growth experiment were erbium (block, 99.9% pure), rhodium (powder, 99.96%), boron (agglomerate, 99.86%) and carbon (block, 99.999%). For one weight part of each solute, 10 weight parts of Cu (block, 99.999%) were used as a flux. The mixture of the solute and flux was placed into a high purity alumina crucible. Purified He gas flowed into the furnace at a rate of 200 mL/min and protected the atmosphere against oxidation. The mixture of the raw materials and flux was heated to 1673 K at a rate of 400 K/h and was held at that temperature for 10 h. The solution was cooled to 1353 K at a rate of 5 K/h and then furnace cooled. The extracted crystals were separated by dissolving Cu in dilute nitric acid. Fig. 1 shows the growth procedure of the single crystals of the quaternary borocarbides in the Er–Rh–B–C system by the flux growth method using molten Cu as a flux. Fig. 2 shows the schematic arrangement of the growth apparatus and vertical temperature distribution of the solution. To search for new compounds, arc-melting syntheses were carried out. The starting materials for the arc-melting syntheses were lanthanide metals (block, 99.9%), rhodium (powder, 99.9%), crystalline boron (powder, 99.86%) and carbon (powder, 99.999%). These elements were mixed in an atomic ratio of 1: 1: 1: 1, 1: 2: 2: 1 and 1: 3: 3: 1 and were arc-melted under a 1 atm argon atmosphere on a water-cooled copper hearth. The solidified button was

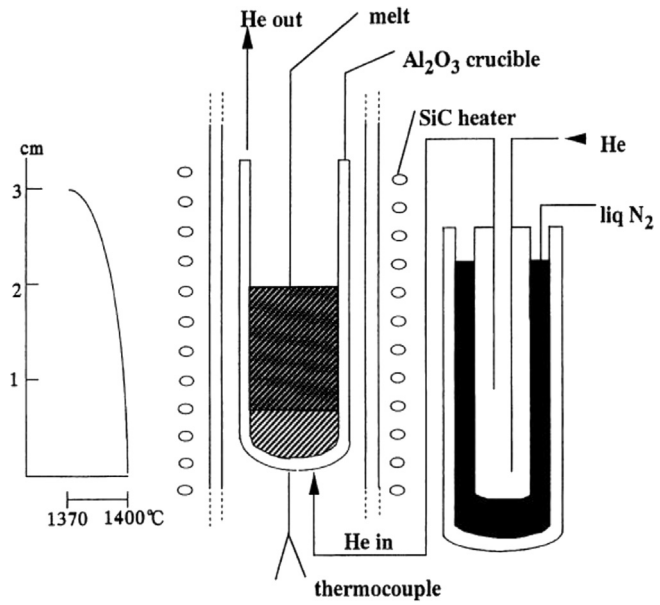

Fig. 2. The geometrical arrangement of the growth furnace and vertical temperature distribution of the solution.

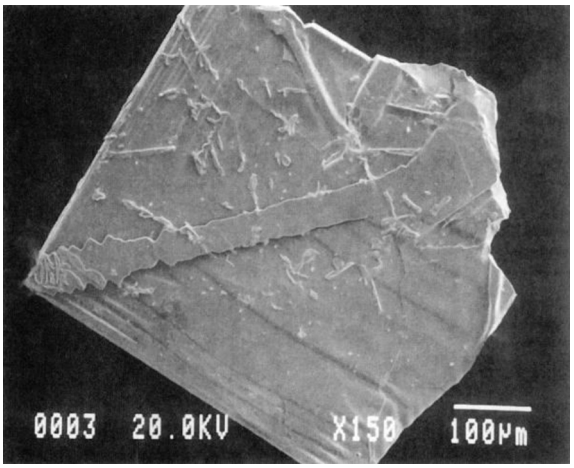

Fig. 3. SEM photograph of a $ErRh_2B_2C$ crystal extracted from the Cu flux.

turned over and re-melted three times to ensure homogeneity.

The morphological properties of the crystals were investigated by electron microscopy (SEM). The chemical composition of the samples was analysed using inductively coupled plasma atomic emission spectrometry (ICP-AES). Crystal structure determination was carried out using an X-ray powder diffractometer, a precession camera, and a four-circle X-ray diffractometer.

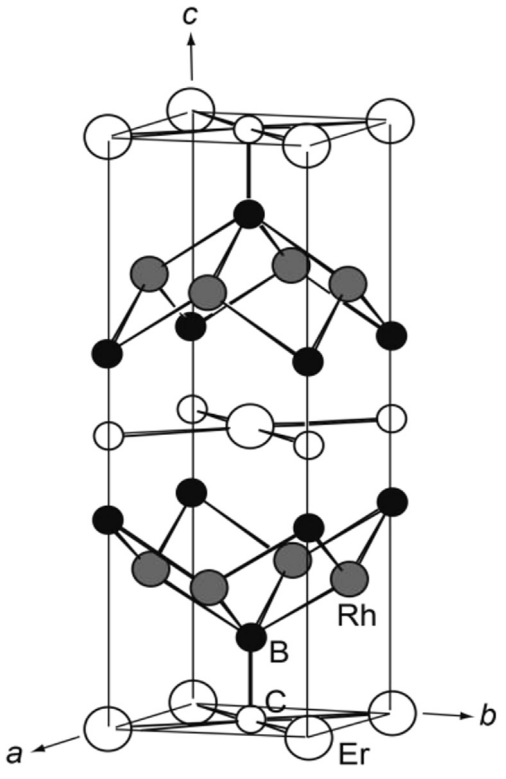

Fig. 4. The crystal structure of $ErRh_2B_2C$.

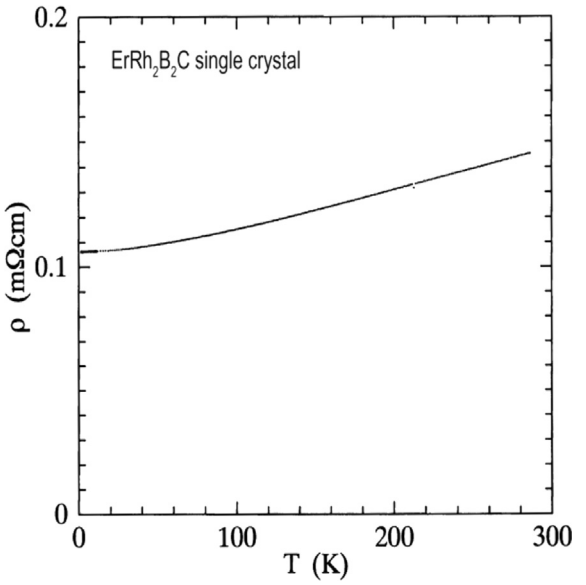

Fig. 5. The temperature dependence of electric resistivity for the $ErRh_2B_2C$ crystal.

Results and discussion

From the solute with the composition of Er: Rh: B: C = 1: 2: 2: 1 and Cu flux, shining golden square-plated single crystals were obtained (Fig. 3).

The results of the chemical analysis for the platy crystals indicate that the chemical formula of the compound is $ErRh_2B_2C$ [3–6]. Other single crystals were co-extracted, mainly hexagonal columnar ones, which were determined to be $ErRh_3B_2$, a known compound. From the other starting compositions, Er:

Table 1
Crystallographic data and electric properties of $ErRh_2B_2C$.

Crystallographic data:	
Chemical formula	$ErRh_2B_2C$
Crystal system	Tetragonal
Structure type	Derivative of $ThCr_2Si_2$ type
Number of molecule per unit cell, Z	2
Lattice parameter	
a (nm)	0.36848(2)
c (nm)	1.05520(3)
Unit cell volume, V ($\times 10^{-28}$ m^3)	1.4327
Electric properties:	
Resistivity at 273 K (mΩcm)	0.147
Resistivity at 4.2 K (mΩcm)	0.107
Residual resistivity ratio RRR	
ρ (273 K)/ρ (1.5 K)	1.38

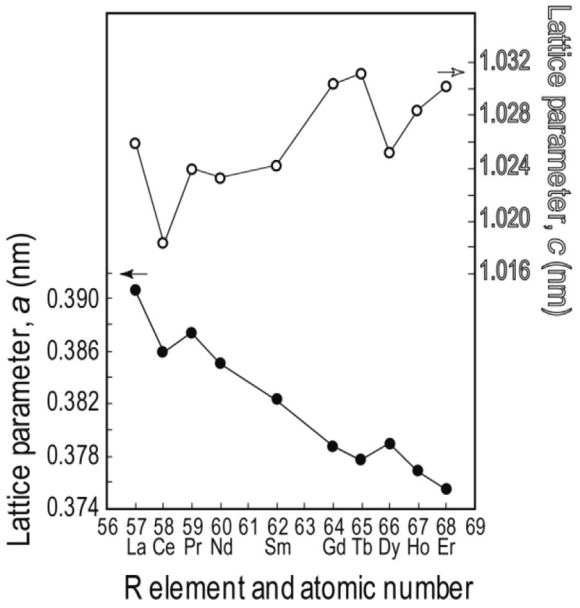

Fig. 6. The lattice parameters of the newly obtained RRh_2B_2C (R = La − Er, except Eu).

Rh: B: C = 1: 1: 1: 1 and 1: 3: 3: 1, the amounts of platy single crystals to the total products obtained were lower. The co-extracted products were mainly hexagonal columnar $ErRh_3B_2$ from 1: 1: 1: 1 and irregularly shaped RhB from 1: 3: 3: 1. $ErRh_2B_2C$ belongs to the tetragonal system based on the $ThCr_2Si_2$ type. Fig. 4 shows the crystal structure of $ErRh_2B_2C$. The lattice parameters of $ErRh_2B_2C$ are a = 0.36848(2) nm and c = 1.05520(3) nm. Structural analysis, with the chemical formula assumed to be $ErRh_2B_2C$, yielded strong reliability factors R = 0.026 and R_w = 0.021. With four probes attached to the flat surface of the (001) plane of the crystal, changes in the electrical resistance with temperature were measured. The compound behaves like a metallic compound (Fig. 5). No superconducting transition is observed down to 1.5 K. The value of the residual resistance ratio ρ (273 K)/ρ (1.5 K) is 1.38. These data are summarised in Table 1.

A search for similar compounds is performed extensively using the arc-melting synthetic method. As a result, we determined that La − Er (except Eu) and Y could form a RRh_2B_2C complex (Fig. 6). The impurity phase RRh_3B_2 increases with decreasing rare earth size. Namely, the size limitation of the formation of the RRh_2B_2C phases was determined to be R = Er. Further characterisations of the newly discovered compounds are in progress.

Conclusions

Single crystals of a new quaternary borocarbide, $ErRh_2B_2C$, were successfully obtained from a molten copper solution. They are shiny golden square plates (up to 1 × 1 × 0.02 mm^3). Structural analysis demonstrates that the compound belongs to a tetragonal system based on the $ThCr_2Si_2$-type with lattice constants a = 0.36848(2) nm and c = 1.05520(3) nm. An investigation of the electrical resistance in the tetragonal (001) plane of the single crystals revealed that the crystals behave metallically. By cooling the crystals to 1.5 K, no superconducting transition is observed. The residual resistance ratio ρ (273 K)/ρ (1.5 K) is 1.38. These data are summarised in Table 1. The range of R, which is produced by the arc melting synthesis, was investigated. It was determined that R = La − Er (except Eu) and Y; the size limitation for the formation of RRh_2B_2C phases was determined to be R = Er. Further characterisations of the new compounds are now in progress [7,8] [9].

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